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PREPARATION AND CHARACTERIZATION OF MEMBERS OF THE SYSTEMS  $\text{Cu(II) MgO/Cu(II)ZrO}_2$

by

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PREPARATION AND CHARACTERIZATION OF MEMBERS OF THE SYSTEMS  
Cu(II)/MgO and Cu(II)/ZrO<sub>2</sub>

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ABSTRACT

Cu(II) is known to prefer square planar or tetrahedral coordination in many oxides. The introduction of Cu(II) in the rock salt or fluorite structures would represent unusual structural behavior and be of interest in catalysis where new oxide supports are being investigated. The systems CuO/MgO and CuO/ZrO<sub>2</sub> were studied and the nature of the products were characterized by x-ray diffraction analysis, temperature programmed reduction studies and magnetic susceptibility. Although some stabilization occurs for Cu(II) in ZrO<sub>2</sub>, a much greater stabilization was observed in the rock salt structure Cu<sub>x</sub>Mg<sub>1-x</sub>O.

MATERIALS INDEX: Copper oxide, Magnesium oxide, Zirconia

Introduction

Gadalla and White have reported (1) on the phase equilibrium relationships in the system CuO-Cu<sub>2</sub>O-MgO. They reported a compound formed with the composition 2CuO · MgO. Drenkhahn and Muller-Buschbaum (2) prepared pure Cu<sub>2</sub>MgO<sub>3</sub> and indicated that it crystallized with an orthorhombic structure (space group Pmmm). However, little has appeared in the literature concerning the substitution of copper for magnesium in the rock salt MgO structure. This is not surprising since Cu(II) does not prefer octahedral coordination.

Cubic ZrO<sub>2</sub> samples containing some transition metal oxides including rhodium oxide (3), iron oxide (4), chromium oxide (5), nickel oxide (6) and cobalt oxide (7) were studied previously in this laboratory. However, there is little published data concerning the introduction of copper into zirconium oxide. It is the purpose of this investigation to study the stabilization of copper oxide towards reduction when copper is inserted into cubic zirconium oxide and also to compare the resulting degree of stabilization with that observed when copper is substituted for magnesium in MgO.

## Experimental

Samples of members of the system  $\text{Cu}_x\text{Mg}_{1-x}\text{O}$  were prepared by the double decomposition of copper(II) nitrate and magnesium nitrate to give compositions between 10 and 30 mole percent calculated as  $\text{CuO}$ . The solution of copper nitrate was prepared by dissolving pure copper metal (99.999% Aesar 10953, Lot 060586) in 16 M nitric acid. The magnesium oxide (Allied Chemical Co. Reagent A.C.S. CODE 1917) was first heated in air at  $800^\circ\text{C}$  for 7 hours and then allowed to cool to room temperature. The appropriate weight of  $\text{MgO}$  was dissolved in the acidic copper nitrate solution. Sufficient nitric acid was added to ensure complete formation of the nitrates. Two ml of water were added for each millimole of total nitrates. The solution was then evaporated on a steam bath to drive off most of the water and then dried at  $150^\circ\text{C}$  for 15 hours. The ground product was decomposed at  $250^\circ\text{C}$  for 5 hrs and then at  $350^\circ\text{C}$  for seven hours. Subsequently, the samples were heated at  $550^\circ\text{C}$  for 24 hours followed by a final heating at  $970^\circ\text{C}$  for 24 hours.

Samples of members of the system  $\text{CuO-ZrO}_2$  were prepared by codecomposition of cupric nitrate and zirconyl nitrate to give compositions containing 10-30 mole percent of  $\text{CuO}$ . The calculated quantities of zirconyl nitrate were added to the solution of cupric nitrate, which was prepared from copper metal. Two ml of water were added for each millimole of total nitrates. The solutions were dried on a steam bath first and then at  $150^\circ\text{C}$  for 15 hrs. The product was ground and heated at  $350^\circ\text{C}$  for 6 hrs and then heated at a temperature at  $550^\circ\text{C}$  for 24 hrs.

X-ray powder diffraction patterns of the samples were obtained using a Philips diffractometer and monochromated high intensity  $\text{CuK}\alpha_1$  radiation ( $\lambda = 1.5405\text{\AA}$ ). The diffraction patterns were taken in the range of  $15^\circ < 2\theta < 85^\circ$  with a scan rate of  $1^\circ 2\theta/\text{min}$  and a chart speed of 30 in/hr. The scan rate used to obtain x-ray patterns for calculation of cell parameters was  $0.25^\circ 2\theta/\text{min}$  with a chart speed of 30 in/hr. Cell parameters were obtained from a least squares refinement of the observed peak positions with the aid of a computer program which corrected for the systematic experimental errors.

The surface areas were measured by the BET method using a Flow Sorb (II) 2300 (Micromeritics Instrument Corp., Norcross, GA). The samples were degassed at  $250^\circ\text{C}$  for 1 hr and the adsorbate gas consisted of a mixture of 30%  $\text{N}_2$  and 70%  $\text{He}$ .

The magnetic measurements were performed on the Faraday balance described by Morris and Wold (8). Honda-Owens (field dependency) plots were also made. Magnetic susceptibilities were measured from liquid nitrogen temperature to room temperature and were corrected for the theoretical core diamagnetism (9).

The temperature programmed reductions of bulk  $\text{CuO}$ , 15 mole %  $\text{CuO/MgO}$  sample, and 15 mole%  $\text{CuO/ZrO}_2$  sample were performed in a Cahn System 113 thermal balance. Before the reductions were started, the samples were preheated in dry Ar up to  $150^\circ\text{C}$ . After the samples were allowed to cool to  $90^\circ\text{C}$  and held at that temperature, the gas was changed from Ar to a 85%Ar/15% $\text{H}_2$  mixture predried over  $\text{P}_2\text{O}_5$ . The flow rate was 60 cc/min. The temperature was then increased to  $1000^\circ\text{C}$  at a rate of  $30^\circ/\text{hr}$ . The weight change vs temperature was recorded.

## Results and Discussion

Samples having the composition  $\text{Cu}_x\text{Mg}_{1-x}\text{O}$  ( $0 < x < .2$ ) were prepared by double decomposition of the nitrates. Complete reaction was achieved at  $970^\circ\text{C}$  and single phase products were identified by x-ray analysis. The final products were yellow and gave cell parameters which did not differ from those of pure  $\text{MgO}$  ( $a = 4.214(2)$ ). At a concentration of 20 atomic percent copper, x-ray diffraction patterns of the product contained impurity peaks of the ternary phase  $\text{Cu}_2\text{MgO}_3$ .

The stability of copper magnesium oxide samples towards reducing atmospheres was compared to that of pure  $\text{CuO}$ . The results shown in Fig. 1 indicate a very large stabilization of  $\text{Cu(II)}$  towards reduction by the sodium chloride structure. Whereas pure  $\text{CuO}$  is completely reduced at  $180^\circ\text{C}$ , the sample of  $\text{Cu}_{.15}\text{Mg}_{.85}\text{O}$  does not begin to reduce until  $885^\circ\text{C}$ .

Magnetic susceptibility vs temperature is plotted in Fig. 2 and shows almost ideal Curie behavior. From this data an effective moment of 1.65 BM for  $\text{Cu(II)}$  was obtained and compares favorably with the spin-only value of 1.73 BM.

Samples of the copper-zirconium oxide system were prepared by the codecomposition of  $\text{Cu(NO}_3)_2 \cdot x\text{H}_2\text{O}$  and  $\text{ZrO(NO}_3)_2$ . X-ray analyses of products containing varying compositions are given in Table 1. All of the products reported in Table 1 were prepared at  $550^\circ\text{C}$ . It was reported by Zhang et al. (10) that decomposition of pure zirconyl nitrate resulted in the formation of tetragonal  $\text{ZrO}_2$  containing a small quantity of monoclinic  $\text{ZrO}_2$ . For the samples prepared by codecomposition of the nitrates, x-ray analysis indicated that  $\text{ZrO}_2$  crystallized with a cubic structure when only 10 atomic percent of copper was introduced into the  $\text{ZrO}_2$ . This is consistent with the results of Collongue (11) who studied the stabilization of cubic  $\text{ZrO}_2$  by various metal ions. It can be seen from Table 1 that there is a decrease in the cell parameter of cubic  $\text{ZrO}_2$  which is consistent with an increase in the copper content of this phase. When attempts were made to prepare cubic zirconium oxide containing 24 atomic percent copper, bulk  $\text{CuO}$  was evident in the x-ray diffraction patterns. Hence, the limit of solubility of copper in  $\text{ZrO}_2$  is below 24 percent.

A sample of  $\text{ZrO}_2$  containing 15 atomic percent copper was heated to  $550^\circ$ , and also to  $600^\circ\text{C}$ . The cubic zirconium oxide remains stable at  $550^\circ\text{C}$ , but at  $600^\circ$  lines of  $\text{CuO}$  and monoclinic  $\text{ZrO}_2$  appear in the diffraction patterns of the products.

TPR (temperature programmed reduction) of pure  $\text{CuO}$  and a sample of  $\text{ZrO}_2$  with 15 atomic percent copper was carried out from room temperature to  $350^\circ\text{C}$ . The results are shown in Fig. 3. It can be seen that pure  $\text{CuO}$  does not begin to reduce until  $135^\circ\text{C}$  whereas the  $\text{CuO/ZrO}_2$  sample begins its reduction at  $105^\circ\text{C}$ . The surface areas of both samples as prepared were determined by the BET method to be less than  $1\text{m}^2/\text{g}$  for  $\text{CuO}$  compared to  $46\text{m}^2/\text{g}$  for  $\text{CuO/ZrO}_2$ . It is not surprising that the sample with the higher surface area should contain  $\text{Cu(II)}$  which is more readily reduced than the  $\text{Cu(II)}$  present in the bulk  $\text{CuO}$ .

sample. Furthermore, the pure CuO is completely reduced at 180°C and the 15% CuO/ZrO<sub>2</sub> is not completely reduced at 350°C.

TABLE 1  
IDENTIFICATION OF PHASES FORMED IN THE Cu(II)/ZrO<sub>2</sub> System

Composition Cu/(Cu+Zr)	Phase	X-ray Parameters	
		a	c/a
0%	Tet ZrO <sub>2</sub> + small am't monoclinic ZrO <sub>2</sub>	5.081(3)	1.02
10%	Cubic ZrO <sub>2</sub>	5.080(3)	
15%	Cubic ZrO <sub>2</sub>	5.067(3)	
20%	Cubic ZrO <sub>2</sub>	5.066(3)	
24%	Cubic ZrO <sub>2</sub> + CuO		

A sample of the 15% CuO/ZrO<sub>2</sub> was x-rayed after being reduced with 85%Ar/15%H<sub>2</sub> at 120°C. Step counting over the (111) reflection of Cu identified the reduction product as metallic copper. There was no evidence for the formation of an intermediate oxide, e.g. Cu<sub>2</sub>O, under these reduction conditions.

Magnetic measurements were also made on zirconium oxide samples containing 15 atomic percent copper. The measurements were made as functions of both field and temperature. All samples showed paramagnetic behavior and have no field dependency at either room temperature or liquid nitrogen temperature. The results of the magnetic measurements are plotted in Fig. 4 as reciprocal susceptibility versus temperature. The measured paramagnetic moment for the sample containing 15 atomic percent copper is 1.91 BM and hence all of the copper is present as Cu(II). The measured Weiss constant of -68 K indicates the presence of antiferromagnetic interactions.

### Conclusions

Copper oxide has been stabilized both in the rock salt structure and in cubic ZrO<sub>2</sub>. The stabilization of Cu(II) is much greater when substituted for magnesium in the system Cu<sub>x</sub>Mg<sub>1-x</sub>O. At concentrations between 15 and 20 atomic percent copper, the ternary phase Cu<sub>2</sub>MgO<sub>3</sub> appears to form. It also appears that cubic zirconium oxide can contain up to 20 atomic percent of copper. The stabilization of Cu(II) when introduced into the rock salt or fluorite structures should be of interest in a number of catalytic processes.

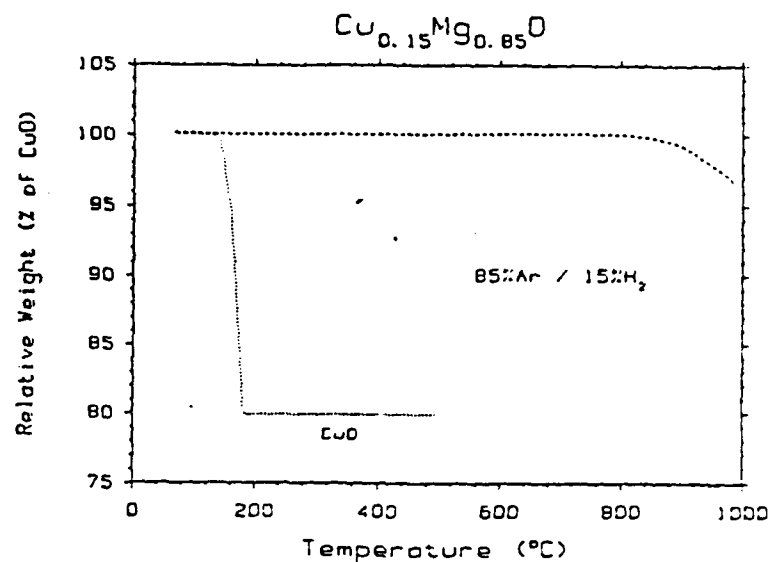


Fig. 1. Loss of weight in 85%Ar/15% $H_2$  as a function of temperature for  $Cu_{0.15}Mg_{0.85}O$  as compared with pure CuO. The weight of MgO was subtracted.

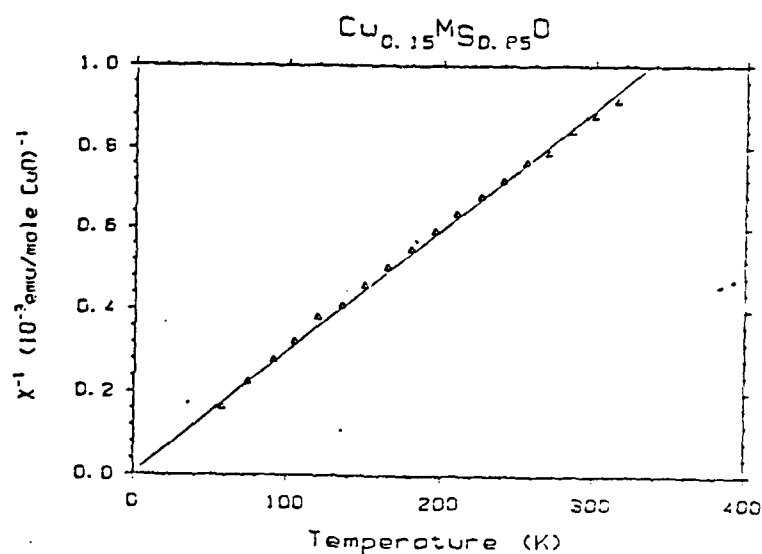


Fig. 2. Temperature dependence of the inverse magnetic susceptibility of  $Cu_{0.15}Mg_{0.85}O$ .

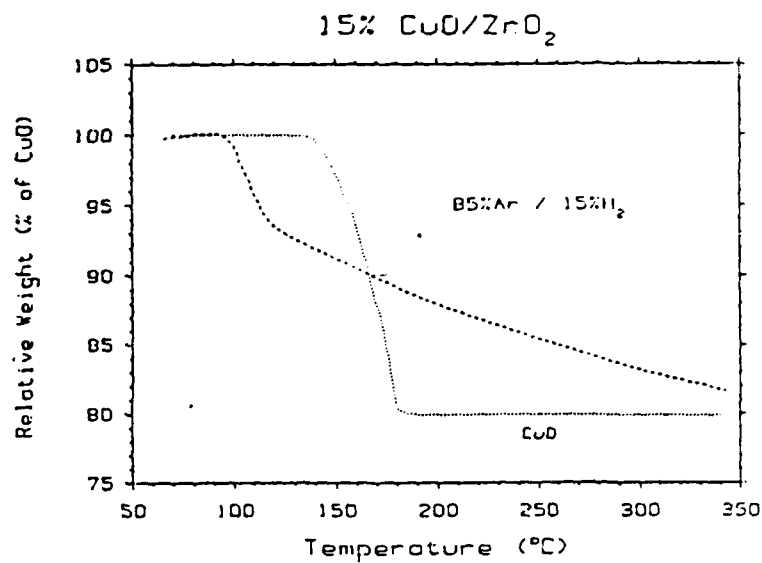


Fig. 3. Loss of weight in 85%Ar/15%H<sub>2</sub> as a function of temperature for 15% CuO/ZrO<sub>2</sub> as compared with pure CuO. The weight of ZrO<sub>2</sub> was subtracted.

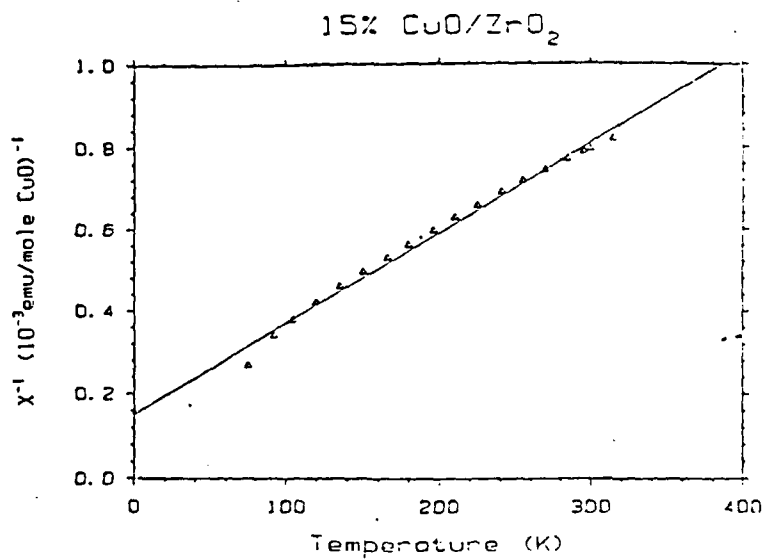


Fig. 4. Temperature dependence of the inverse magnetic susceptibility of 15% CuO/ZrO<sub>2</sub>.



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